

# **A Multiscale Molecular Modeling Understanding of CO<sub>2</sub> Storage in Porous Materials**

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With the rapid increase of the global population and the industrialization of more and more countries, the consumption of energies explosively growing. Currently over 85% of the global energy demand is being supported by the burning of fossil fuels [1]. Carbon dioxide capture and storage (CCS) is a three-step process including CO<sub>2</sub> capture, a process consisting of separating CO<sub>2</sub> from other emissions before it enters the atmosphere; CO<sub>2</sub> transportation to a storage site; and its permanent storage. However, the considerable cost of capture, approximately two thirds of the total cost for CCS (primarily separating CO<sub>2</sub> from other gases), is slowing down the deployment of commercial CCS projects. In the majority of the proposed technologies, one significant contributor to lower cost is the maximum separation efficiency that can be achieved by a given capture material. Thus, the discovery of new materials with high separation ability becomes one of the biggest challenges. In the past two decades, a new class of crystalline porous materials, metal-organic frameworks (MOFs) has emerged, research into which has developed into one of the most prolific areas in chemistry and materials science today [2-4]. MOFs are comprised of metal-containing nodes linked by organic ligand bridges assembled principally through strong coordination bonds. The crystallinity of MOFs also allows precise structural characterization by diffraction methods, thus facilitating their rational design and the formulation of structure–function relationships.

Advances in computational power have allowed molecular simulation to play an important role in identifying properties and potential applications. By providing microscopic information that sometimes is not accessible or difficult to obtain with experiment, simulations complement experiment. Simulations also play an important role on the rational design of new materials (e.g., MOFs) for specific applications. Based on these advantages, computer simulations have been used to study MOF properties, including CO<sub>2</sub> adsorption and separation.

In this study MOF Cu-BTC was investigated with grand canonical Monte Carlo simulations. Two microdomains with different electrostatic field strengths, tetrahedron-shaped pockets and square-shaped pores were identified. Each Monte Carlo simulation involved four types of movement of adsorbents to achieve equilibrium: insertion, deletion, displacement, and rotation. The results were then averaged.

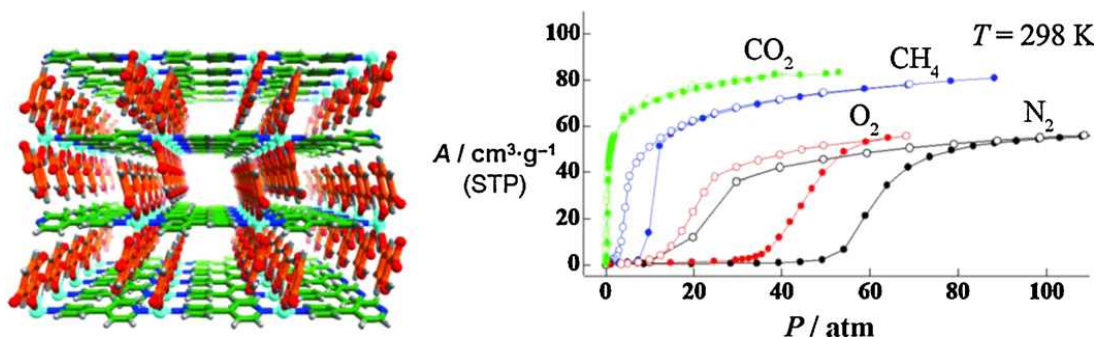


FIG. 1. The MOF model (a) and adsorption isotherm (b)

With a series of simulations at different pressures, adsorption isotherms can be obtained by relating the chemical potential and gas phase pressure through an equation of state. The loading of CO<sub>2</sub> in comparison to CH<sub>4</sub>, O<sub>2</sub> and N<sub>2</sub> was monitored by calculating their isotherms and comparing with experiment. Once the amount of loading was identified, the conformations were optimized using density functional theory to determine the electronic structure and figure out the influence of the MOF structure on adsorption behavior and differences in amount of loading. Interaction energies between gas molecules and MOFs were also obtained using DFT methods, as in comparison with force-field models first-principles calculations better describe the non-bonded interactions between gas molecules and MOFs leading to more accurate predictions of adsorption properties. These interactions can later be fitted to an appropriate potential function to obtain force-field parameters. These can then be used in a larger scale dynamics study to look into the flexibility of the lattice under gas pressure. Such a workflow is expected to become a valuable tool in the design of materials for CCS.

## References

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